# **PCBs** in the Bluestone River





#### TITLE

## PCB TMDL SOURCE ASSESSMENT STUDY, BLUESTONE RIVER WATERSHED

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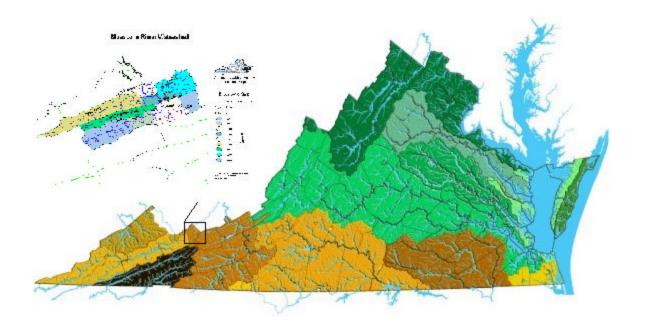
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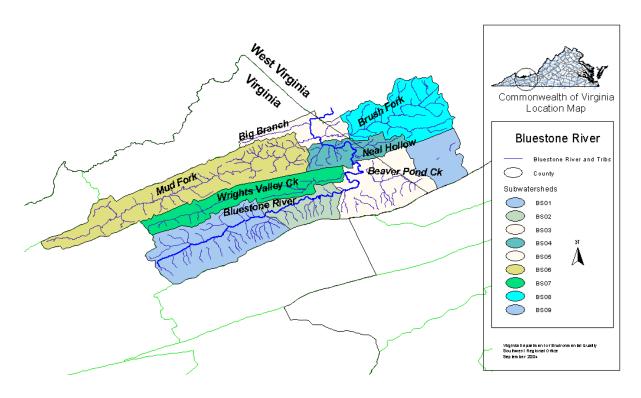
#### **ABSTRACT**

The Department of Environmental Quality (DEQ) has completed a polychlorinated biphenyl, (PCB) source assessment study for the Bluestone River Watershed in Virginia. This watershed is located within the "Coal Fields" of Virginia and West Virginia where some reports indicate over 300 mining industry related facilities existed. See Figure 1, map of the region. Many of these either used or handled PCB oils. The task of source assessment was made more difficult since many operations have either closed, were located in the remote mountainous valleys and ridges of the watershed, or were operated as home-based industries. The goals of the Bluestone study were to ensure that no site is actively contributing PCBs to the watershed and to provide basis for the PCB Total Maximum Daily Load (TMDL) study required by the Clean Water Act. One of the innovative aspects of the project was the use of semi permeable membrane devices (SPMDs) to determine the contribution of PCB from the major tributaries to the Bluestone.

FIGURE 1&2. Map of Bluestone River Watershed; a subset of Virginia



### **Bluestone River Watershed**



The study resulted in locating two sites that will require remedial PCB activities. Both sites are located in the State of West Virginia. USEPA and the West Virginia Department of Environmental Protection (DEP) will direct the cleanup efforts. The DEQ activities in the

watershed had some other benefits such as prompting the removal of trash and metal from the stream bank, removal of barrels full of oily fluids, the repair of a broken sewer line along the stream, and the development of a new local Bluestone River conservation organization.

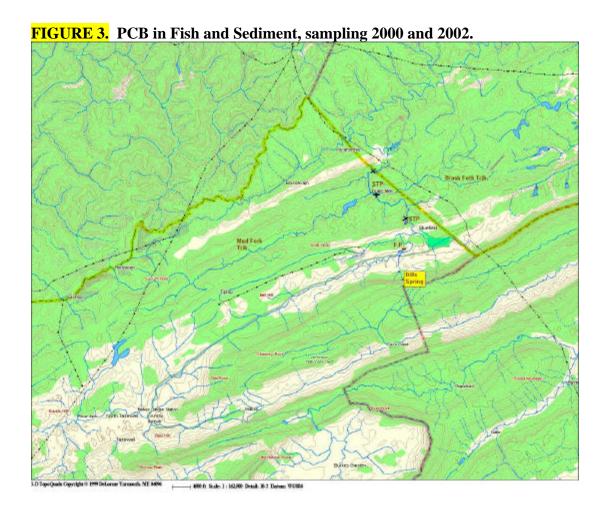
#### PROJECT DISCUSSION

Several factors complicated the Bluestone River Watershed PCB Source Assessment Study: 1) Most misuse of PCBs occurred decades ago. 2) The watershed is dissected by the Virginia, West Virginia State Line. Tributaries from industrial areas in West Virginia enter Virginia and ultimately the Bluestone exits Virginia into West Virginia. Therefore, DEQ worked closely with the State of West Virginia Department of Environmental Protection (DEP) and the USEPA. 3) Two surface water intakes supply drinking water to the Virginia portion of the watershed. Citizens and agencies were concerned about the impacts to these potable water sources. 4) Karst geology moved water from the surface through underground pathways near known PCB contaminated sites. 5) PCB transport mechanisms and bioaccumulation interactions are different in each watershed and even within a subwatershed.

Over the past several years, the Commonwealth of Virginia has developed an approach for evaluation of state waters for Persistent Bioaccumulative Toxins, PBTs, such as methyl mercury and PCBs. The first step is a study of the extent of contamination in each state watershed by testing one or more samples of fish and sediment at very low concentration levels. The congener analytical method has been used for PCBs. When a high level of PCBs was found in the Bluestone River, in both fish and sediment, a second more intense study was implemented.

#### **Source Assessment Efforts**

During the first phase, the Bluestone River was sampled in two locations for fish and sediment in August, 2000. The results came back demonstrating a significant PCB contamination level at the state line and decreased amounts in the same species at the further upstream sampling location. Various fish species were sampled and indicated different levels of uptake based upon many factors including their feeding habits, size/age, bioaccumulation and metabolic rates, fat content, habitat temperature, etc. The historic VDH advisory level for PCB contamination in fish tissue is 600 (ug/kg) ppb in edible fillets. The highest concentration found in the first round of PCB in fish sampling of this watershed was 2,368 ppb in a composite of 3 carp. This sample was taken south of the VA and WV state line at Yards, VA. As a result of the initial findings, the Virginia portion of the Bluestone River was posted by the Virginia Department of Health, VDH, with a fish consumption advisory for carp, for most of its fishable waters (Figure 4). Although the original Bluestone River fish consumption advisory was based upon 600 ppb, the VDH is in the process of dropping the level to 50 ppb of total PCB in edible fish fillets.



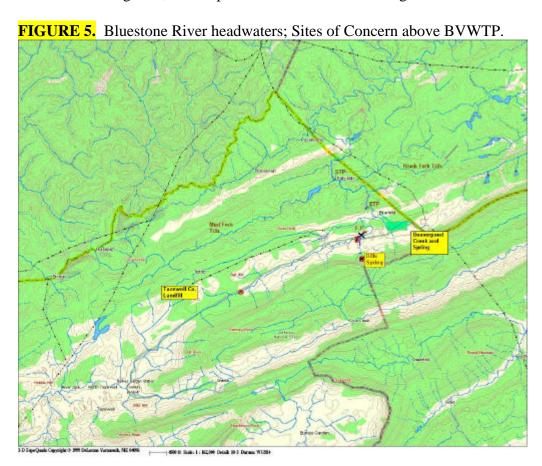
# **VDH Fish Advisory --PCB**

- Bluestone River at the Route 460 bridge crossing south of Bluefield downstream to the Virginia/West Virginia state line near the town of Yards in Tazewell County
- Carp caught in these waters should not be consumed. (8/6/01)
- <a href="http://www.vdh.state.va.us/HHControl/fishing\_advisories.htm">http://www.vdh.state.va.us/HHControl/fishing\_advisories.htm</a>



In response to these findings, DEQ initiated a source assessment study to locate potential sites that are contributing PCBs to the watershed. The study included the following elements:

1) Involvement of the Stakeholders from the Watershed: One of the initial steps in the evaluation of the watershed, involved enlisting the aid of the stakeholders in the watershed. These are persons who knew or could find out about the historical PCB related activities in the watershed. The watershed stakeholders were informed of the data and the PCB source assessment study with public notices and two TMDL meetings for the bacterial and benthic impairments in the Fall and Winter, 2003. Through discussions with the stakeholders, it became apparent that there was much public concern and stress over the potential health problems from drinking water intakes. The VDH Bluestone River fish consumption advisory was based upon the finding of PCBs in fish tissue above the VDH standard. However, few people are thought to consume fish from the Bluestone watershed above the recommended frequencies. Many more residents rely on the drinking water produced at the Bluefield Virginia Water Treatment Plant, BVWTP, which has the intake located within an impaired segment listed for fish consumption due to PCBs. Figure 5, is a map of Bluestone River showing sites of concern above the BVWTP.



**2)** Investigation of the contamination of the Potable Water Supply: In response to public concerns, sampling was performed to evaluate the raw water and potable water at the BVWTP for presence of PCBs. VDH coordinated the low level drinking water analysis effort. This testing revealed that the PCB levels in the drinking water were not detected, compared to the maximum contaminant levels for potable water as defined by the regulations supporting the Safe Drinking Water Act.

DEQ performed support sampling efforts at the request of VDH, both at and upstream of the raw water intake on both fish tissue and sediment. Fish may range upstream of the raw water intake, but downstream travel is obstructed by a 6 foot spillway just below the intake. The carp and other fish species which were collected, were several years old and would have represented an average exposure through time and weather events.

Coordination was done with VaDGIF (Virginia Department of Game and Inland Fisheries), the DEQ Sampling and Monitoring group, and local residents, to sample fish at the intake reservoir and take sediments from strategic locations above the water supply (see Figures 6 & 7). This follow up sampling event occurred October 2003. The fish tissue data revealed that carp had 300 ppb of PCBs. The sediment results indicate fairly low concentrations in various locations above the drinking water source, ranging from 0.32 ng/g at the BVWTP to 8.97 ng/g upstream on the mainstem. Even if fish in the reservoir were exposed to a concentration in the sub ppb (ng/g) range, evidence supports that these low levels are enough to reach PCB concentration levels in the fish above the edible fish tissue consumption advisory level of 50 ppb.

FIGURES 6 & 7. Bluestone Virginia Water Treatment Plant Fish Sampling with VDGIF.





3) Research Existing Records: Research was performed on existing records of PCB related activities of state and federal agencies. These records include PCB complaints, spills, emergency responses, etc. Several lists were generated including one of property owners in the watershed using the Tazewell County tax map. Another list was made of current and historic businesses related to PCB oil activities, which included anecdotes of PCB misuse on private residential or public properties. Next, records of historical PCB activities were researched and reviewed from various EPA websites including the EnviroMapper, CERCLA-Superfund, and TRI sites. Additionally, research was performed on activities from VaDEQ PREP files, VaDEQs Waste Program files, WVDEP, WVDHHR, EPA On-Scene Coordinator (OSCs), Bluefield Fire Department, and Virginia Office of Emergency Services. Among the information compiled were PCB sampling schemes, data, and in some cases reports of activity, cleanups, and site closures in the watershed. Many of the regulatory and responsible authority contacts had responded personally to historic PCB related events in the Bluestone watershed.

**4) Collect Stakeholder Information:** During the fourth task, potential sources were identified by personal contacts and results of survey forms to gain information about historic PCB usage in the watershed. Contacts with the stakeholders in the watershed were the primary source of information leading to several contaminated sites.

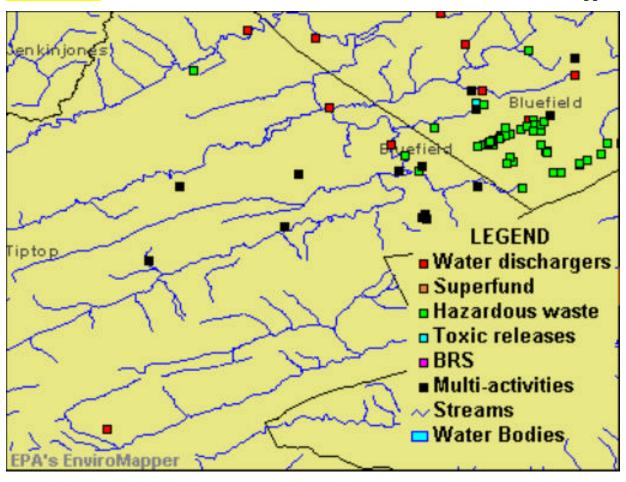
The Bluestone River PCB Source Assessment survey consisted of a two-page questionnaire, which was tailored mainly toward industry and reporting of industrial activities (Figure 8). A second version of the survey was developed to communicate with stakeholders in the watershed who were not related directly to industrial PCB activities (Figure 9). Over one hundred fifty surveys were handed out or mailed out in the Bluestone River watershed in Virginia and West Virginia to industries, local historians, and residents of the watershed. Approximately 20 percent of the surveys were returned.

FIGURES 8 & 9. Bluestone River Watershed PCB Source Assessment Survey Forms; Industrial and Generic Stakeholder.

- Click here for the Bluestone River PCB Source Investigation Survey
- <u>Click here</u> for the Bluestone River PCB Source Investigation Stakeholder Survey

An important aspect of this project was the personal contact with the stakeholders to supplement the information that was provided with the forms. DEQ visited all the industries along the Virginia sections of the stream bank to obtain information and prompt completion of the forms. The personal visits to these industries was very labor intensive but was critical to obtaining the information about the PCB use in the watershed. Figures 10 and 11 indicate the sites of concern from EPA's EnviroMapper program, and feedback from the Source Assessment surveys.

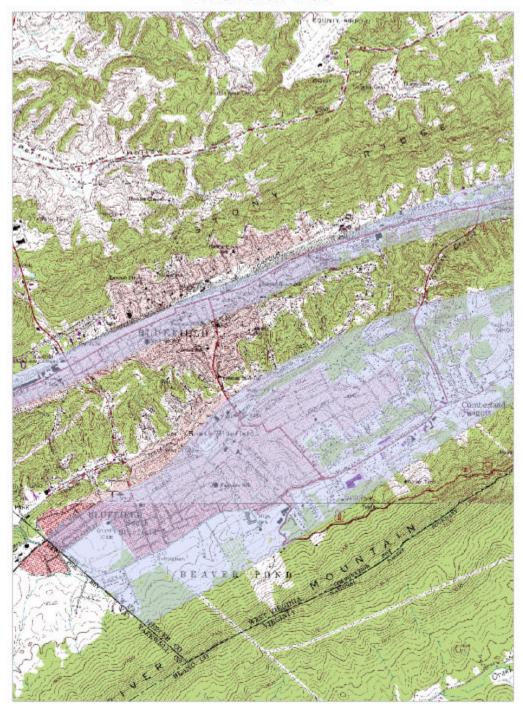
FIGURES 10. Bluestone River Watershed PCB Sites of Concern (USEPA EnviroMapper).



**5)** Research Underground Water Movement: The fifth task was researching the Karst influences on PCB transport in the Bluestone River watershed, including both surface and subsurface water flows. Understanding the movement of surface water as it enters sinkholes and caves and knowing where the water re-emerges on the surface became important since some of the potential and known historical PCB use sites are upgradient of sinkholes where surface flow is transported underground. It is well known that surface drainage re-emerges into some of the larger springs in the watershed: Beaverpond Resurgence Spring, Big Spring, Little Spring, and various other springs. On this portion of the study, DEQ conferred with the following geological experts for their resources and understandings of water transport: VaDMME, VDOT, WVDOT, and WVDEP mining hydrologists.

FIGURE 11. Map indicating some of the Karst regions of the watershed.

# Bluefield Area



One of the sites of concern, called Hart Electric Corporation facilities, had surficial flows that drained into a sinkhole on adjacent property. The Hart Electric Corporation was known to have spilled PCB oil, buried drums of used PCB oil, and baked out the transformer coils in their facility. When it became a CERCLIS - Superfund cleanup site in the 1980s, contamination was extensive. The structure was removed and some soil was excavated and replaced. The sinkhole that received flows from this property, was dye tested to determine the flow retention and discharge location(s). The dye emerged within several hours in Beaverpond Creek. Researching the underground flows from Hart Electric was important since it was feared that PCB contamination had been transported by this underground stream to Dill Spring, which is a source of potable water for the BVWTP. During the survey of the hydrology it was discussed that the drainage from West Virginia probably does not extend down to Dill Spring because of a rise in the underground geology south of the Beaverpond Resurgence. DEQ performed sediment sampling at Dill Spring and the results confirmed that only extremely low PCB concentrations were present.

Another area of concern was the older industrialized section along the railyards of Bluefield WV. This industrial section includes several previously investigated PCB sites. An interesting aspect of water movement is that both surficial and storm system drainage directs water into Beaverpond Creek, a tributary to the Bluestone. However, the Karst formation directly underground of the railyard, appears to drain into an adjacent watershed, the East River. PCB contamination from this industrial area or seepage from the old storm drainage system could migrate to either the Bluestone or East Rivers.

Third and fourth areas where underground water movement is important to potential PCB transport are located in the Abbs Valley and Town of Pocahontas Valley. Neither of these areas was originally considered a potential contributor to the PCB issue in VA. However, the geological research and responses to the surveys revealed underground transport to VA waters. Pollutants can be transported via these underground pathways from the deep mines of the Pocahontas formation into the Bluestone watershed. The mining operations used many pieces of equipment that contained PCBs including transformers and heavy mining hydraulic equipment. It is widely reported that mining operations disposed of spent fluids in the mines. A common routine maintenance practice for hydraulic mining machinery was to discharge these fluids from the equipment onto the mine floor. The deep mine drainage is to Laurel Fork, a tributary to the Bluestone downstream in West Virginia. Although Laurel Fork was not included in the original DEQ impaired stream segment, this information provided the basis for an expanded study in this watershed by EPA.

A second 'Big Spring' in NeMours West Virginia, drains Abb's Valley, where survey responses indicated that a home operation baked out used transformer coils and reclaimed the copper. This type operation typically generates dioxin and PCB soil and water contamination. This site is being evaluated by both EPA and the VDH since there is a potable water intake for the Town of Pocahontas within one half mile downstream.

### 6) Coordination with Interstate and Federal Agencies for Sediment Sampling:

Additional sediment and soil sampling was performed at approximately 44 sites in the watershed after PCB survey form responses were reviewed. DEQ worked with WVDEP and USEPA to design the sampling plan and EPA contracted the actual sampling and analysis. Results indicated that one site previously cleaned up by EPA has significant contamination remaining in storm drains that flow toward the Bluestone River. This contamination may have been contributed by the industrial operation that occupied the site following the original EPA cleanup. Just downstream of the discharge of the contaminated storm drain, PCBs were not detected, providing confusing results.

Another site, which was identified through the survey responses, had both PCB and dioxin contamination around EPA response levels. Except for these sites, the sediment in the Bluestone River and at several other sites measured below detection limits, around 50 to 80 ppb of PCBs, when they were tested using the Arochlor method. One potential problem with using the PCB Arochlor method is that weathered samples yield variable results. If the ratios of the primary quantification/identification congeners were significantly different than the original Arochlor ratios, then the sample may indeed have total PCB congener concentration above the TSCA cleanup concentration, yet not be identified as having PCBs.

7) Semi-Permeable Membrane Device Study: DEQ wished to determine the PCB loading by the various tributaries in the watershed in order to determine the total maximum daily loads (TMDLs) for the watershed. Semi-Permeable Membrane Device (SPMDs) were selected as the appropriate sampling device. The study design includes deployment of SPMDs at two times during the year, at seasonal high and low streamflows. The SPMDs are called 'virtual fish' for their ability to uptake chemicals such as PCBs and accumulate them with measurable kinetics that can be used to calculate the levels of contamination in a water body. The SPMDs uptake only the dissolved fraction which is the readily bioavailable form.

FIGURE 12. Photograph, SemiPermeable Membrane Device Triolein Fish Oil in Polyethylene 'Lay Flat' bags.

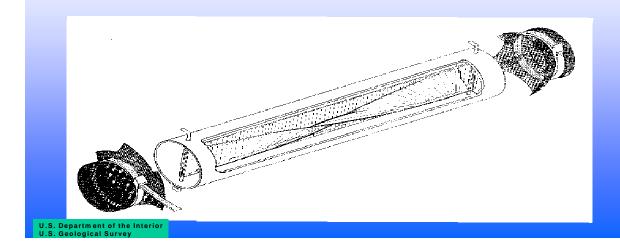


# **FIGURE 13.** Horizontal Deployment apparatus for SPMDs.

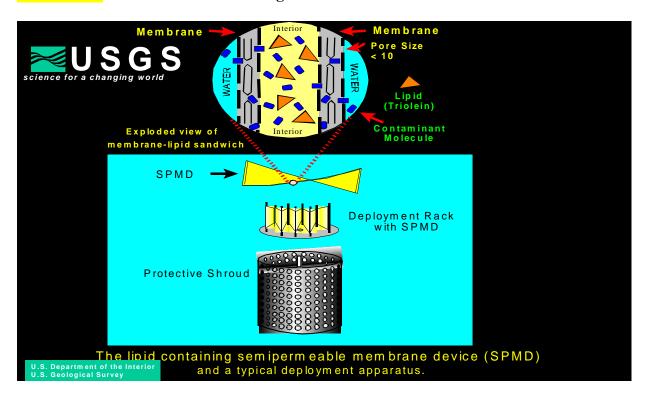
## A HORIZONTAL DEPLOYMENT APPARATUS FOR SPMDs

Designed by Jon Lebo, of CERC





# FIGURE 14. SPMD Crossectional Diagram.



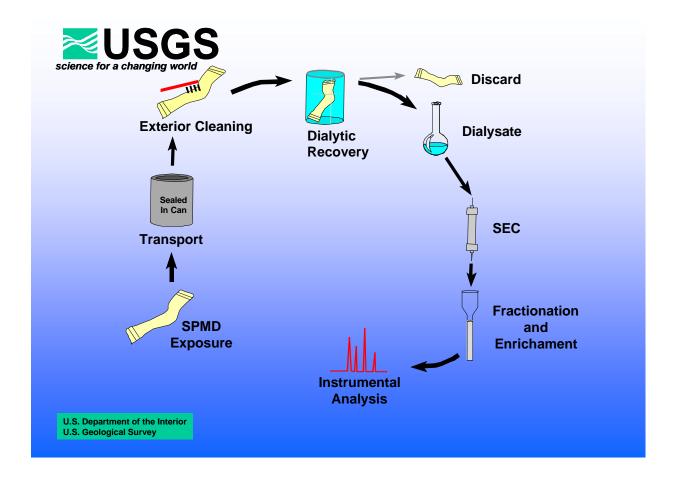
# FIGURE 15. Photograph, SPMD Example of a Protective Shroud.





U.S. Department of the Interior U.S. Geological Survey

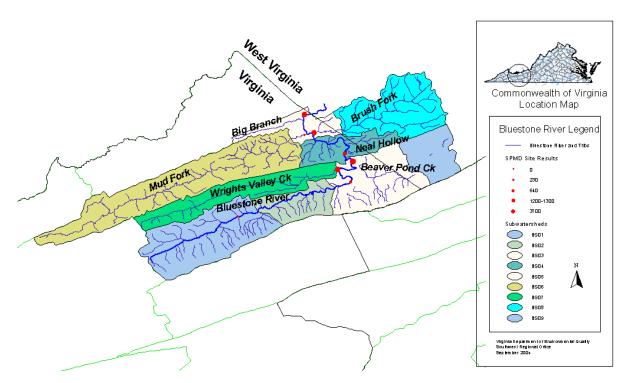
FIGURE 16. SPMD Analytical Process Diagram.



In this study, SPMDs were deployed during the high seasonal flow period in March 2003. The deployment for the low seasonal flow period is scheduled for November or December, 2004. Sampling locations were chosen to isolate loadings from different sources in the watershed, and met depth and mixing requirements for the devices.

In the Winter, 2004, eight locations were selected for SPMD deployment. Six of the original eight devices survived the observation term and were sent to the laboratory for analysis. After exterior cleaning of the SPMD tapes, the removed surficial algae and debris, were recombined with the other fractions for cleanup and extraction. The results were then background corrected and all QC samples were evaluated for loss of the deuterated compounds and presence of PCBs. All the quality control checks met specifications and were background corrected for contamination, then the sample results were deemed valid. The samples were analyzed by the congener high resolution GC/MS method according to USGS CERC and then summed for total PCBs. The corrected results were in units of nanograms of PCBs per SPMD tube. The USGS uptake rate chemical kinetic studies were used to convert the results into the approximate water column concentration of PCBs. The water column results were reported in units of picograms per liter.

## Bluestone River Watershed Spring 2004 SPMD Site Results



### FIGURE 18. SPMD Deployment in Bluestone River Watershed.



Sample deployment locations were selected to represent various areas within the watershed. The first location selected was the public water supply for the Town of Bluefield, VA to help answer the health risk exposure concerns. Survey responses indicated several potential sources above the drinking water intake, if the WTP had been contaminated. The second site, Camp Joy, was selected upstream of the filtration plant uptake for two reasons: 1) A more upstream sample above the WTP would either provide a clean reference site and eliminate some potential sources above the device, or 2) help pinpoint the contamination source. The third site was located in Wright's Valley Creek, just above the confluence with the Bluestone. A foundry located on the banks of Wright's Valley Creek was reported to historically take metal parts for melting that might have contained or been coated with PCB oils. Another facility nearby, repaired mining machinery and appeared to have large quantities of oil in the ground at multiple locations. The fourth sampling site was in Beaverpond Creek, just above the confluence with the Bluestone River. The Beaverpond Creek location was critical for various reasons. Three known EPA Superfund cleanup sites, two PCB and one dioxin, were located on the drainage; as well as stakeholders reports of additional suspicious PCB activity sites. The fifth site was the sewage treatment plant. Sludge from the BVWTP was flushed down to the STP. This could dramatically increase the amount of PCBs this site could have if the BVWTP were effectively

removing PCB laden particulates from river water. Additionally, there were reports of various industrial practices, such as pouring barrels of PCB contaminated oils down the storm and sewer drains. Some sewer pipes might continue to release PCBs dumped years ago from their contaminated linings. The sixth sampling site was selected upstream of Brush Fork confluence with the Bluestone River. Brush Fork is just above a second Virginia Sewage Treatment Plant, STP, and this STP by this tributary and Mud Fork. Contamination from various transformer maintenance shops which operated historically up this valley in West Virginia would be trapped in the SPMD located in Brush Fork. Mud Fork, the seventh sampling site, provided a drinking water source to much of Bluewell, WV, however it doesn't have industrial development or much reported reputation for contamination. The eighth sample location was along the mainstem of the Bluestone River just before the river crossed into West Virginia at Yards.

**8) Evaluation of Results:** Two of the samples deployed in April of 2004, Camp Joy and Mud Fork, had to be redeployed because they were either removed from the stream intentionally during stream cleaning, or washed partially up onto the bank during storm events. The quality control checks were all well within specifications and all field and trip blanks were clean. The remaining sample results indicate the highest contamination level at Beaverpond Creek. This site had a water column concentration 3,700 pg/L, more than two times the surface water standard for PCBs, 1,700 pg/L. The second level of contamination was 1,200 to 1,300 for sites three, six, and eight. The next level of contamination was 640 pg/L measured at the STP. The lowest level of contamination was measured at the BVWTP at 230 pg/L.

After the PCB congener results were tabulated, the data were plotted in elution order format using a line graph and compared against known unweathered manufacturer specifications for the original arochlor mixtures. The Ballschmitter system was used to assign congener identification and to help develop plots. Each result was evaluated and determined to be mostly one Arochlor or combinations of several different Arochlor mixtures. Using flow results the loading from the different tributaries were estimated from the high flow period and will be used to help develop a Total Maximum Daily Loading for PCBs in this watershed.

SPMDs have several advantages over fish or other biological tissue analysis. They remain in one location (hopefully) during a specific sampling period. They remain for 20 to 30 days, providing an average of conditions that fish might have been exposed to in that water body during the same period. Not only does the SPMD provide a time averaged uptake that mimics the fish exposures, but it allows determination to some degree, of the particular Arochlor or mixture of Arochlors. Various mixtures of Arochlors might be present in the region of contamination, and SPMD results demonstrate better accuracy than previous methods of analysis, which may involve mobile targets such as fish or sediments. Interpretation of the Arochlor ratios depends upon what occurred to the oil mixture during metabolism and weathering. One of the problems with analyzing fish is that not only does the fish metabolize the PCB but the ratios of the congeners may change as some of the compounds become dechlorinated. Additionally, the fish contain more interfering compounds than an algae covered polyethylene tube. The connection to one location allows the contaminants to be correlated to flow and temperature conditions, which vary within a watershed and affect the chemical kinetics of uptake and loss across the membrane. Extensive kinetics studies have been done by various research organizations on most of the PCB congeners to compare the effects of temperature, flow, and other environmental conditions upon uptake.

Disadvantages of the devices include that they may be lost or damaged by powerful flows or storm events, and that converting SPMD results into 'calculated total water concentrations' depends upon scientific interpretation of theoretical partitioning. These equations estimate the equilibrium between the dissolved and particulate fractions of a chemical. The calculations provide results, based upon previous research into real world partitioning situations.

Lateral mixing depends upon the flow regime of each location and may not necessarily have been optimal during lower flow conditions. Although sites were carefully selected, lateral cross-sections of PCB concentrations in the water column were not assessed and may introduce

variability into the results. Water column loading values from this study are considered estimates.

FIGURE 19. SPMD Based Water PCB Concentrations in Bluestone River Watershed.

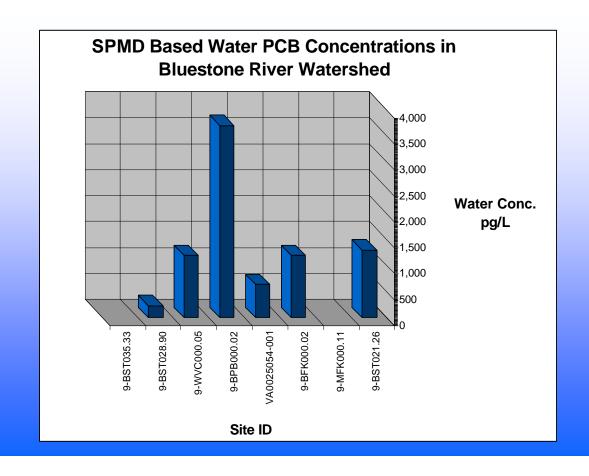
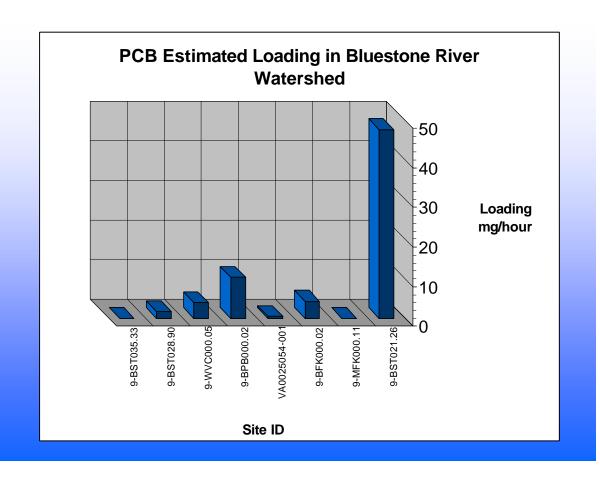


FIGURE 20. SPMD Based PCB Loading Rates in Bluestone River Watershed.



#### **Future Efforts and Goals**

The original study design included sampling in lower flow conditions. Possible relocation of some SPMDs is being considered based on the contamination levels of the first round of high flow conditions. For example, if Camp Joy and Mud Fork have low concentrations, the devices could be moved to suspect hot spots on Beaverpond Creek drainage. Additionally, the Sewage Treatment Plant may not be sampled in the low flow conditions. Currently, USEPA, Virginia Department of Health, West Virginia Department of Environmental Protection, and West Virginia Department of Health and Human Resources are considering options of contributing SPMDs to further enhance the study of the watershed, simultaneous to the DEQ efforts.

The redeployment of SPMDs during low flow conditions will include one additional sample for air analysis. Historically, transport mechanisms in some watersheds include up to 90 percent of PCB transport through air.

The exercise of investigating PCBs in the Bluestone River watershed has thus far resulted in the discovery of two contaminated sites currently being evaluated by EPA for cleanup prioritization. Additionally, another site has been reported and will be sampled in the near future. The public water supply for Pocahontas, VA is being studied for potential health risks. One broken sewer line was discovered, reported, and repaired. Several barrels of oil were removed from the stream, after being discovered during SPMD deployment. The barrels may have been washed downstream during recent floods. Perhaps most importantly, questions of drinking water quality at the Town of Bluefield, Virginia, have been answered with several different sets of low-level analyses including the SPMDs. Follow up to help better pinpoint the locations of the contamination in the watershed may reveal additional cleanup sites or provide other alternatives to improving the quality of water, sediment, fish, and recreational activities in the Bluestone River Watershed.

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